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An application of accelerator mass spectrometry in geochronology

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MEASUREMENT OF COSMOGENIC $^{36}\text{Cl}/\text{Cl}$ IN YOUNG VOLCANIC ROCKS:
AN APPLICATION OF ACCELERATOR MASS SPECTROMETRY IN GEOCHRONOLOGY

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Abstract

We have measured $^{36}\text{Cl}/\text{Cl}$ ratios in a number of young volcanic rocks in order to test the feasibility of using ^{36}Cl buildup as a geochronometer for materials less than about 700,000 years old. All of the analyzed rocks have been dated independently using K-Ar or other radiometric dating methods and have exposure histories that are known or can be reasonably assumed. Measured $^{36}\text{Cl}/\text{Cl}$ ratios in these rocks are in good agreement with the calculated in-situ ^{36}Cl buildup curve. These analyses indicate that AMS measurement of ^{36}Cl buildup in young rocks is a potentially powerful new method for dating materials that had previously been undatable, and as such will have broad applications in volcanology, tectonics, geophysics, and Quaternary research.

Introduction

The dating of young volcanic rocks is a geological problem that has not been satisfactorily resolved. A number of methods have been used for dating relatively old rocks, but techniques for rocks less than 500,000 years old have not been as successful. Rocks in the 10,000-100,000 year range have been analysed using a number of techniques, including K-Ar (Dalrymple, 1967), fission-track (Naeser, 1979), radiocarbon (Lockwood and Lipman, 1980), $^{40}\text{Ar}/^{39}\text{Ar}$ (di Brozolo and others, 1981), and uranium-series disequilibrium (Allegre, 1968) but in many cases these have yielded equivocal results. Moreover, these methods are not applicable to all young volcanic rocks, due to restrictions on the types of materials suitable for dating.

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The commonly used radiometric dating techniques mentioned above are of two general types. One, of which K-Ar is an example, utilizes the buildup of daughter products of primordial radionuclides; the other, exemplified by standard ^{14}C dating, uses the decay of cosmogenic isotopes that are produced in the atmosphere and then incorporated into terrestrial reservoirs. This study investigates a third approach, the measurement of cosmogenic radionuclides in geological materials exposed to cosmic rays at the surface of the earth. While the first two techniques measure the time since an object to be dated became a closed geochemical system, the third method measures the time of exposure at the surface. Therefore, this method has the potential for dating features which are currently undatable, such as geomorphic surfaces, as well as determining the exposure age of volcanic rocks.

The use of light, rare isotopes such as ^{36}Cl has been considered for dating young materials for some time (Davis and Schaeffer, 1955; Lal and Peters, 1962). However, levels of these isotopes on the earth are quite low, and it has only been since the development of accelerator mass spectrometry (AMS) that an analytical method sensitive enough for practical analysis has been available. Recently, ^{36}Cl studies have been applied to groundwater (Bentley and others, 1984) lacustrine sediments (Phillips and others, 1983) and geothermal systems (Phillips and others, 1984), but have not been applied to the dating of igneous rocks.

Cosmogenic ^{36}Cl Buildup Dating

^{36}Cl has several characteristics which made it a prime candidate for buildup dating. It builds up to measurable levels relatively quickly since the product element (chlorine) is present in most rocks only in trace quantities; ^{36}Cl activities produced by nuclear processes within rocks, due to the decay of uranium and thorium, are much lower than the cosmogenic activity after only a few thousand years of exposure; and the mobile, hydrophilic nature of chlorine aids in the separation of in-situ produced ^{36}Cl from that derived from an atmospheric (meteoric) source. Recent research (Kimura and others, 1983) has shown that even relatively immobile radionuclides can penetrate rocks in geologically short time periods. Since ^{36}Cl is more hydrophilic than either ^{10}Be or ^{26}Al - two other candidates for

use in buildup dating (Nishiizumi and others, 1986) - this feature is useful in cases where it is necessary to separate in-situ and meteoric radionuclides. Most ^{36}Cl in rocks is produced by thermal neutron activation of ^{35}Cl ; a second method of production, important mainly in rocks with low chlorine content, is direct spallation of ^{36}Cl from ^{40}Ca and ^{39}K . Spallation from titanium and iron is insignificant at the earth's surface due to attenuation by the atmosphere of the highly energetic cosmic rays necessary for these reactions. Calculation of the spallation production rate is discussed in Yokoyama and others (1972) and representative values for spallation production are given in Yokoyama and others (1977). Negative muon capture by ^{40}Ca (Kubik and others, 1984) and neutron activation of ^{39}K are minor reactions that produce ^{36}Cl . Although potentially significant at depth, these reactions may be ignored in calculations for surface rocks.

Cosmogenic isotopes accumulate at a rate proportional to the exposure time of the material; at the same time, they decay at a rate proportional to their decay constants. The measured ^{36}Cl content of a rock (usually expressed as the ratio of the number of atoms of the ^{36}Cl to the number of atoms of stable chlorine) is thus a function of the production rate, decay rate, and initial element content of the rock (Bentley and others, 1985), given as:

$$(^{36}\text{Cl}/\text{Cl})_m = ([\text{ED}(\text{PR})]/\lambda^{35}\text{Cl})(1 - \exp(-\lambda t)) + (^{36}\text{Cl}/\text{Cl})_0 \exp(-(\lambda t)) \quad (1)$$

where

λ = decay constant

t = time in years

PR = production rate of ^{36}Cl

^{35}Cl = number of atoms of ^{35}Cl

E = factor accounting for elevation of sample site

D = factor accounting for depth of sample below surface

and the subscripts (m) and (0) refer to measured and initial ratios, respectively.

The E term corrects for the attenuation of cosmic rays in the atmosphere; tables for this correction are given in Yokoyama and others (1977). Lal and Peters (1967) provide D, the depth correction for subsurface samples.

Sampling

In order for Equation (1) to be applied to surface exposure dating in a straightforward manner, the material to be dated should have been completely shielded from cosmic-ray exposure until exposed suddenly at the surface. Volcanic rocks admirably meet these conditions, and there are enough very young rocks that have been dated by conventional methods to provide a sufficient number of calibration samples. Hence these are an ideal subject for a test of a cosmogenic isotope buildup chronometer. Our samples include young volcanic rocks that are fresh, relatively dense and impermeable to groundwater, located at high elevations that will provide maximum cosmic-ray flux, and have been dated by reliable methods with ages that are compatible with the observed geology of the sample site. Also, wherever possible, samples were collected through a vertical section at a given site in order to allow evaluation of the variation of cosmogenic isotope production rates with depth below the ground surface. In addition to the isotopic measurements, these samples were analysed petrographically and geochemically so that the calibration suite would be fully documented. The rocks collected from the several localities within the arid regions of New Mexico and southeastern California are our primary suite of calibration samples; those samples collected from the more humid regions of California and the Pacific Northwest comprise a secondary group.

Preparation and analysis

The samples were prepared by splitting to remove any surface rind and then crushed and sieved to <100 mesh. The ground samples were leached with deionized water to remove adsorbed meteoric chloride. After leaching, the rock powders were digested by total fusion with NaOH and dissolved in deionized water. Chloride was precipitated from this

solution as AgCl by addition of an excess of AgNO₃. Since ³⁶S is an interfering nuclide in AMS analysis of ³⁶Cl, the AgCl was carefully purified by repeated dissolution in NH₄OH and reprecipitation with HNO₃. ³⁶Cl/Cl ratios were determined using the TAMS at the Nuclear Structure Research Laboratory at the University of Rochester (Elmore and others, 1979). Whole-rock major and minor element analyses were performed by x-ray fluorescence and neutron-activation analysis at the Los Alamos National Laboratory.

Results

Since the analysed rocks were collected at different locations and elevations and are of different chemical compositions, all measured ³⁶Cl/Cl ratios were normalized to sea-level cosmic-ray flux and an arbitrary reference composition. Normalized ratios are shown relative to the predicted buildup for the reference composition on Figure 1. The values were normalized by:

$$\frac{[(^{36}\text{Cl}/\text{Cl}) - (^{36}\text{Cl}/\text{Cl})_0] (^{35}\text{Cl}/^{37}\text{Cl})_r [K_2O(PR_K)_r + CaO(PR_{Ca})_r + Cl(PR_a)_r]}{[K_2O(PR_K) + CaO(PR_{Ca}) + Cl(PR_a)] (ELD)} \quad (2)$$

Reference compositions were 165 ppm Cl, 2.35 weight per cent K₂O, and 5.00 weight percent CaO. Samples from depth were normalized using their density as measured by specific gravity and a half-attenuation length of 132 g/cm² (Nishiizumi and others, 1984). The production rates for ³⁶Cl from spallation of K and Ca were 2670 atoms/kg per %K₂O, and 710 atoms/kg per %CaO (Yokoyama and others, 1977). The reference production rate of ³⁶Cl by neutron activation of ³⁵Cl was 81 atoms/year per ppm Cl, based on a sea-level neutron flux of 10⁶ neutrons/kg per year (Lal and Peters, 1967).

Discussion

Our results show that ³⁶Cl/Cl increases with sample age in a predictable manner. Several of the samples, mainly rocks of rhyolitic composition, have higher values than expected. Since our early work

indicated that these samples were not contaminated with meteoric "bomb" ^{36}Cl , these high values suggest that the cosmogenic nuclide production rates that we have been using may be in error. In comparison, the values for the near-surface basalts compare well with the predicted curve. As the rhyolites have a significantly higher K content than the basalts (4-5% K_2O vs. 1-2% K_2O), it would appear that the production rate for ^{36}Cl from K could be higher than published values. We have been using rates extrapolated from data on the spallation production of ^{22}Na from Al (Yokoyama and others, 1977); it may be that the $^{39}\text{K}(n,\alpha)$ reaction is more important at near-surface levels than previously realized. Also, several of the basalts sampled at depth have similarly higher ratios than expected, which suggests that the muon-induced production of ^{36}Cl from Ca may likewise be significant for these rocks. Indeed, Kurz (1986) reported muon-induced production of ^3He to be the dominant mechanism for production of this isotope at depths below 170 g/cm^2 , and the same may be true for ^{36}Cl . However, it will be necessary to accumulate more data before these production rates can be fully evaluated. In addition to our data for volcanic rocks, preliminary $^{36}\text{Cl}/\text{Cl}$ analysis of granitic boulders from Tioga-age (10,000-20,000 years b.p.) moraines from the Sierra Nevada (Phillips and Jannik, unpub. data) indicate that buildup dating will be applicable to this type of material as well.

Summary

^{36}Cl analyses have been obtained for a number of well-dated young volcanic rocks as part of an evaluation of the use of this isotope as a dating tool. Although uncertainties remain in the interpretation of our data, it is apparent that there is a predictable buildup of ^{36}Cl with time, produced in-situ since the emplacement of these flows at the surface. We expect that, with refinement, ^{36}Cl buildup can be used to date surface-exposure ages for volcanic rocks and other surficial materials. The ability to directly date very young materials of a wide range of compositions, such as archeological artifacts, glacial moraines, geomorphic surface, and soils, as well as volcanic rocks, will constitute a powerful tool for many of the earth sciences.

References cited

- Allegre, C.J., 1968, ^{230}Th dating of volcanic rocks: a comment; Earth and Planetary Science Letters 5, 209-210.
- Bentley, H.W.; Phillips, F.M.; Davis, S.N., in press, Chlorine-36 in the Terrestrial Environment; in: Fritz, P., and Fontes, J.-C., (eds.), Handbook of Environmental Geochemistry; Elsevier, Amsterdam.
- Dalrymple, G.B., 1967, K-Ar ages of Recent rhyolites from the Mono and Inyo Craters, California; Earth and Planetary Science Letters 3, 289-298.
- Davis, R., Jr., and Schaffer, O.A., 1955, Chlorine-36 in nature; Annals of the New York Academy of Science 62, 5, 105-122.
- di Brozolo, F.R.; Huneke, J.C.; Papanastassiou, D.A.; and Wasserburg, G.J., 1981, ^{40}Ar - ^{39}Ar and Rb-Sr age determinations on Quaternary volcanic rocks; Earth and Planetary Science Letters 53, 445-456.
- Elmore, D.; Fulton, B.R.; Clover, M.R.; Marsden, J.R.; Gove, H.E.; Naylor, H.; Purser, K.H.; Kilius, L.R.; Beukens, R.P.; and Litherland, A.E., 1979, Analysis of ^{36}Cl in environmental water samples using an electrostatic accelerator; Nature 277, 22-25.
- Kimura, K.; Saito, Y.; Sabanai, M.; Hirao, Y.; Sato, J.; and Sato, K., 1983, Apparent penetration of fallout ^{137}Cs into rocks in Izu-Oshima; Geochemical Journal 17, 303-305.
- Kubik, P.W.; Korschinek, G.; Nolte, E.; Ratzinger, U.; Ernst, H.; Teichmann, S.; and Morinaga, H., 1984, Accelerator mass spectrometry of ^{36}Cl in limestone and some paleontological samples using completely stripped ions; Nuclear Instruments and Methods in Physics Research B5, 326-330.
- Kurz, M.D., 1986, In situ production of terrestrial cosmogenic helium and some applications to geochronology; Geochimica et Cosmochimica Acta 50, 2855-2862.
- Lal, D., and Peters, B., 1962, Cosmic ray produced isotopes and their application to problems in geophysics; in: J.G. Wilson and S.A. Wouthysen, (eds.), Progress in Elementary Particle and Cosmic Ray Physics; John Wiley, New York; 1-74.
- _____ 1967, Cosmic ray produced radioactivity in the earth; in: K. Sitte, (ed.), Handbuch der Physik; Springer-Verlag, New York; 46/2, 551-612.

- Lockwood, J.P., and Lipman, P.W., 1980, Recovery of datable charcoal from beneath young lavas: lessons from Hawaii; *Bulletin Volcanologique* 43-3, 609-615.
- Naeser, C.W., 1979, Fission-track dating and geologic annealing of fission tracks; in: W.C. Jager and J.C. Hunziker, (eds.), Lectures in Isotope Geology; Springer-Verlag, New York, 154-169.
- Nishiizumi, K.; Elmore, D.; Ma, X.Z.; and Arnold, J.R., 1984, ^{10}Be and ^{36}Cl profiles in an Apollo 15 drill core; *Earth and Planetary Science Letters* 70, 157-163.
- Nishiizumi, K.; Lal, D.; Klein, J.; Middleton, R.; and Arnold, J.R., 1986, Production of ^{10}Be and ^{26}Al by cosmic rays in terrestrial quartz in situ and implications for erosion rates; *Nature* 319, 134-136.
- Phillips, F.M.; Smith, G.I.; Bentley, H.W.; Elmore, D.; and Gove, H.E., 1983, ^{36}Cl dating of saline sediments: Preliminary results from Searles Lake, California; *Science* 222, 925-927.
- Phillips, F.M.; Goff, F.; Vautaz, F.; Bentley, H.W.; Elmore, D.; and Gove, H.E., 1984, ^{36}Cl as a tracer in geothermal systems: Example from Valles Caldera, New Mexico; *Geophysical Research Letters* 11, 1227-1230.
- Yokoyama, Y.; Reyss, J-L.; and Guichard, F., 1977, Production of radionuclides by cosmic rays at mountain altitudes; *Earth and Planetary Science Letters* 36, 44-50.
- Yokoyama, Y.; Sato, J.; Reyss, J.; and Guichard, F., 1973, Variation of solar cosmic ray flux deduced from ^{22}Na and ^{26}Al data in lunar samples; *Proceedings of the 4th Lunar Science Conference*; 2, 2209-2227.

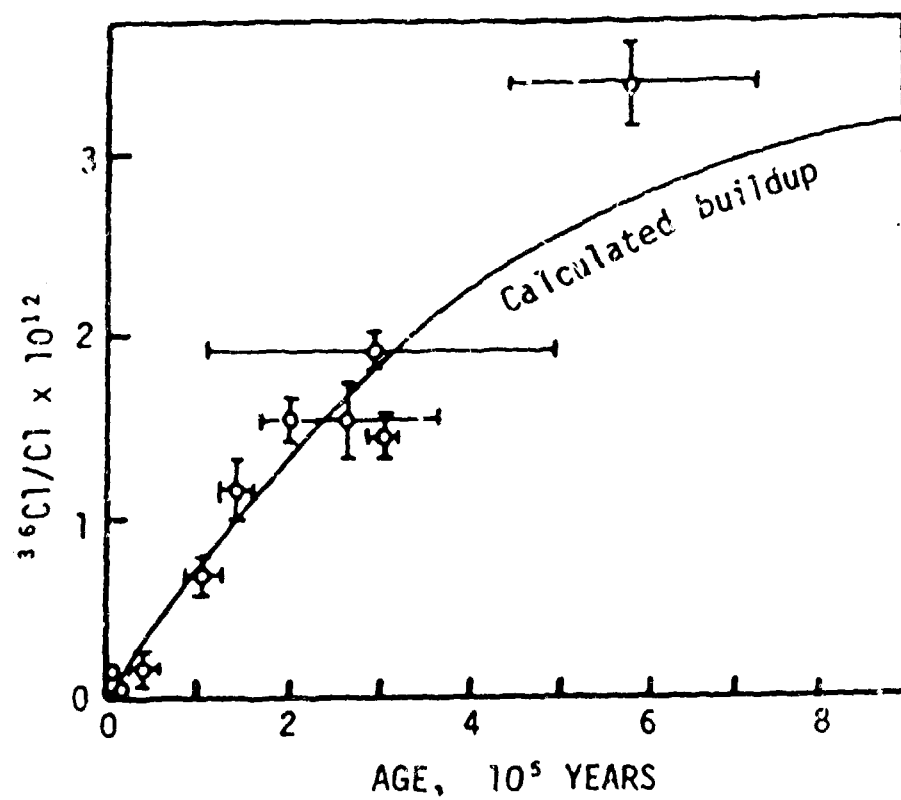


Figure 1: Normalized $^{36}\text{Cl}/\text{Cl}$ in calibration samples
vs. published ages of sampled flows.